

Europäisches Patentamt European Patent Office Office européen des brevets



(1) Publication number : 0 407 098 B1

(12)	EUROPEAN PATEN	IT SPECIFICATION
(45)	Date of publication of patent specification : <b>16.02.94 Bulletin 94/07</b>	(51) Int. CI. <sup>5</sup> : <b>C08L 21/00,</b> C08L 23/02
21	Application number : 90307096.9	
22	Date of filing : 28.06.90	
54	Composition for injection molding.	
30	Priority : 28.06.89 JP 163645/89 28.06.89 JP 163646/89	<ul> <li>Proprietor : NIPPON PETROCHEMICALS COMPANY, LIMITED</li> <li>3-1, Uchisaiwaicho 1-chome Chiyoda-ku Tokyo (JP)</li> </ul>
43	Date of publication of application : 09.01.91 Bulletin 91/02	
45	Publication of the grant of the patent : 16.02.94 Bulletin 94/07	<ul> <li>(72) Inventor : Aida, Fuyuki</li> <li>1-30-3, Higahsi-Mukojima, Sumida-ku</li> <li>Tokyo (JP)</li> <li>Inventor : Miyazaki, Masaaki</li> <li>3-35-2 Okubo</li> <li>Konan-Ku, Kanagawa-ken (JP)</li> </ul>
84)	Designated Contracting States : DE FR GB IT	Inventor : Miyamoto, Tsutomu 2-262, Hayao, Tone-cho Kitasoma-gun, Ibaregi-ken (JP)
56	References cited : EP-A- 0 227 163 EP-A- 0 269 265 EP-A- 0 324 278 AU-B- 511 385 US-A- 4 049 616 US-A- 4 244 861 US-A- 4 247 474	<ul> <li>(74) Representative : Cropp, John Anthony David e al MATHYS &amp; SQUIRE 10 Fleet Street London, EC4Y 1AY (GB)</li> </ul>
		the mention of the grant of the European patent, any

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

#### Description

#### Background of the Invention

- The present invention relates to a composition for injection molding and a composition for vehicular exterior 5 material. More particularly, the present invention is concerned with a composition for injection molding and a composition for vehicular exterior material both containing a partially crosslinked product prepared by dynamically heat-treating an  $\alpha$ -olefin (co)polymer having 2 to 8 carbon atoms and a rubbery substance as well as, if necessary, an inorganic filler and/or a softening agent in the presence of a specific crosslinking agent and a
- polyfunctional monomer. The compositions of the present invention are well-balanced in rigidity, impact resis-10 tance, appearance of molded products and moldability, and are employable for baskets and bamboo baskets for documents sorting, kitchen use, dressing room use, fruits and refuse, for lids of various things of daily necessities, namely, for caps of wide-mouth bottles, toy parts, and also for vehicular exterior materials such as rear finisher, sill, rear coater panel, engine hood, trunk lid, fender, door panel, protector, bumper fascia, energy absorber, air spoiler, side molding, weather strip, shock absorber, dust boots, vacuum connector, rack and pin-
- 15 ion boots, and mud guard.

Thermoplastic elastomer (TPE) is mentioned as one of those commonly used heretofore as thermoplastic resins for injection molding. Above all, olefinic thermoplastic elastomers are used frequently because they are inexpensive.

- 20 Generally, such olefinic thermoplastic elastomers are blends each comprising as a hard segment a crystalline polypropylene (hereinafter referred to simply as "PP") or polyethylene and as a soft segment an ethylene- $\alpha$ -olefin copolymer rubber, e.g. ethylene-propylene rubber (hereinafter referred to simply as "EPR") or ethylene-propylene-diene random copolymer rubber, or an olefinic elastomer such as polyisobutylene or polybutadiene. Partially crosslinking is often conducted for the improvement of physical properties.
- For example, in Japanese Patent Laid-Open No.41950/1979 there is disclosed a composition prepared 25 by kneading PP and EPR with polyethylene having a density of 0.915 to 0.97 and peroxide. Further, in Japanese Patent Laid-Open No.139445/1980 there is proposed a composition comprising PP, EPR, a high-density polyethylene and talc, and in Japanese Patent Laid-Open Nos.42643/1993 and 80335/1983 there is proposed a composition comprising PP, EPR and a linear ethylene- $\alpha$ -olefin copolymer.

30

40

45

55

The conventional processes for the preparation of such injection molding compositions are broadly classified into the following two.

The first process is a mere blending of a thermoplastic resin with a rubbery substance. This process involves problems such as deterioration of mechanical characteristics and of heat resistance, ineffective improvement of impact resistance, and poor appearance of molded products such as the presence of weld mark and flow mark.

35

According to the second process, an organic peroxide is added at the time of kneading of a thermoplastic resin and a rubbery substance to enhance the effect of improving mechanical characteristics as compared with that obtained in the aforementioned simple blending. Thus, an organic peroxide is used in this process, so when a peroxide degradation type resin such as polypropylene is used as the hard segment, there rapidly occurs thermal decomposition of the organic peroxide, with the result that a molecular cutting reaction is unavoidable,

thus leading to deterioration in mechanical characteristics such as flexural modulus and yield tensile strength. In the case of using a peroxide crosslinking type resin such as polyethylene, a crosslinking reaction of the

hard segment proceeds and fluidity is deteriorated markedly, resulting in that the moldability is deteriorated to the extent of molding being difficult, and in order to ensure good moldability it is necessary to use an extremely small amount of an organic peroxide. Thus, the handling is difficult.

Anyhow, even in a crosslinking reaction using a peroxide, deterioration of mechanical characteristics is unavoidable as in the foregoing simple blend; besides, the surface appearance of a molded product obtained is inferior, such as the presence of weld mark or flow mark.

Recently, the use of TPO for injection molding has been expanded to the automobile industry, i.e., auto-50 mobile parts, and at the same time performance conditions required have been more and more diversified.

For example, as to automobile exterior materials, not only high heat resistance and low-temperature impact resistance but also good moldability, product appearance and coatability are required. It is difficult for conventional thermoplastic elastomers (TPE) to satisfy all of these requirements. Particularly, with conventional TPE's, the balance between low-temperature impact resistance and the surface appearance of molded products, such as whether weld mark or flow mark is present or not, is still unsatisfactory.

Particularly, where the inorganic filler is a metal oxide (or hydroxide), the receptivity of polyolefin resins is low and the dispersibility is poor, so molded products obtained are inferior not only in the appearance thereof but also in the mechanical characteristics thereof. To avoid this, it is necessary to add a soft substance or a high molecular compound having a polar group.

Thus, the thermoplastic resin compositions for injection molding prepared by the above conventional processes are not fully satisfactory in practical use, so the provision of an improved and superior composition is desired.

EP 0324278 describes a process for preparing a thermoplastic resin composition by dynamically heattreating a mixture of a thermoplastic resin substantially containing no olefinic unsaturated carbon-carbon bond and an elastomer having an olefinic unsaturated carbon-carbon bond in the presence of a dihydroaromatic compound or a polymer thereof as cross-linking agent.

10 The present invention has been accomplished in view of the above-mentioned points and it is an object thereof to provide a composition for injection molding well balanced in mechanical characteristics, appearance of a molded product obtained using the composition and moldability, and having improved compatibility with thermoplastic resin compositions and inorganic fillers, by using a partially crosslinked product prepared by dynamically heat-treating an α-olefin (co)polymer and a rubbery substance in the presence of a special cross-

linking agent and a polyfunctional monomer, and, if necessary, also using an inorganic filler and/or a softening agent, all in specific proportions.

It is another object of the present invention to provide a composition for vehicular exterior material of high performance superior in low-temperature impact resistance and having a beautiful surface appearance, which composition is constituted by a thermoplastic resin composition containing a partially crosslinked product ob-

20 tained by dynamically heat-treating a specific amount of a polypropylene resin, or a polyethylene resin if desired, and a rubbery substance in the presence of a special crosslinking agent and a polyfunctional monomer, or such thermoplastic resin further containing a softening agent and/or an inorganic filler.

# Summary of the Invention

25

40

55

15

5

Having made extensive studies along the above-mentioned objects, the present inventors found out that a molded product not deteriorated in mechanical characteristics as compared with the results obtained by the conventional crosslinking using organic peroxides, and remarkably superior in the surface appearance free of weld mark or flow mark, is obtained by using a thermoplastic resin composition containing a partially cross-

- 30 linked product prepared by dynamically heat-treating a thermoplastic resin and a rubbery substance in the presence of a specific compound such as a dihydroaromatic compound or a polymer thereof as a crosslinking agent and a polyfunctional monomer, or such thermoplastic resin composition further incorporating therein a softening agent and/or an inorganic filler. In this way we accomplished the present invention.
- More specifically, in one aspect of the present invention there is provided an external component for a vehicle which is molded from a composition comprising a partially crosslinked product prepared by dynamically heat-treating:
  - (A) 40-90 wt% of an  $\alpha$ -olefin (co)polymer resin having 2 to 8 atoms;
  - (B) 10-60 wt% of a rubbery substance;

(C) 0.01-7 parts by weight of a polyfunctional monomer based on 100 parts by weight of the components (A)+(B); and

0.01-7 parts by weight, based on 100 parts by weight of the components (A)+(B), of at least one crosslinking agent selected from:

(D) a dihydroaromatic compound or a polymer thereof;

- (E) an ether compound;
- 45 (F) a tetrahydroaromatic compound, and

(G) a cyclopentane compound.

The component preferably additionally comprises:

(H) 1-30 parts by weight of a softening agent;

(I) 1-100 parts by weight of an inorganic filler; or 1-30 parts by weight of a softening agent and 1-100 parts

50 by weight of an inorganic filler;

based on 100 parts by weight of the partially crosslinked product.

The  $\alpha$ -olefin (co)polymer (A) having 2 to 8 carbon atoms is preferably at least one of polyethylene resins, polypropylene resins and poly-1-butene resins.

The  $\alpha$ -olefin (co)polymer (A) having 2 to 8 carbon atoms more preferably comprises: (A-1) 40-90% by weight of a polypropylene resin, and (A-2) 0-30% by weight of a polyethylene resin, provided the total amount of Al+A2 is in the range of 40% to 90% by weight.

The rubbery substance (B) is preferably an ethylene-propylene random copolymer rubber or an ethylenepropylene-diene random copolymer rubber.

The dihydroaromatic compound (D) is preferably a 1,2-dihydroquinoline compound or a polymer thereof,

or 9,10-dihydrophenanthrene; the ether compound (E) is preferably dihydropyran or isopropenyl acetate; the tetrahydroaromatic compound (F) is preferably 1,2,3,4-tetrahydronaphthalene, tetrahydrobenzene, or tetrahydrofuran, and the cyclopentane compound (G) is preferably indene.

The polyfuncational monomer (C) is preferably a bismale imide compound or a di(meth) acrylate compound and the softening agent (H) is preferably at least one of paraffinic, naphthenic and aromatic petroleum distillates and synthetic oils.

In the second aspect of the present invention there is provided a composition suitable for use in an external component of a vehicle comprising a partially crosslinked product prepared by dynamically heat-treating:

(A) 40-90 wt% of an  $\alpha$ -olefin (co)polymer resin having 2 to 8 carbon atoms;

(B) 10-60 wt% of a rubbery substance;

(C) 0.01-7 parts by weight of a polyfunctional monomer based on 100 parts by weight of the components (A)+(B); and

0.01-7 parts by weight, based on 100 parts by weight of the components (A)+(B), of at least one crosslinking agent selected from: 15

(E) an ether compound,

5

10

20

30

(F) a tetrahydroaromatic compound, and

(G) a cyclopentane compound.

The composition preferably additionally comprises:

(G) 1-50 parts by weight of a softening agent;

(H) 1-100 parts by weight of an inorganic filler; or

(I) 1-50 parts by weight of a softening agent and 1-100 parts by weight of an inorganic filler based on 100 parts by weight of the partially crosslinked product.

#### 25 **Detailed Description of the Invention**

The present invention will be described in detail hereinunder.

As examples of the  $\alpha$ -olefin (co)polymer (A) having 2 to 8 carbon atoms used in the present invention, there are mentioned homopolymers of  $\alpha$ -olefin such as polyethylene, polypropylene, poly-1-butene, poly-4methylpentene-1 and polyhexene-1, as well as intercopolymers of such  $\alpha$ -olefins.

More particularly, there may be used such polyethylene resins as high and medium density polyethylenes, high pressure process low-density polyethylenes, linear low-density polyethylenes, very-low density polyethylenes, ethylene-unsaturated carboxylate copolymers, and ethylene-carboxylic acid unsaturated ester copolymers; such homopolymers as isotactic polypropylene and syndiotactic polypropylene; propylene-ethylene

35 block copolymer, and propylene-1-butene copolymer. These polymers may be used each alone or as mixtures. Particularly, polypropylene resins (PP) are preferred because they are inexpensive and well balanced in various physical properties such as mechanical characteristics, e.g. rigidity, heat resistance, and the appearance of molded products, e.g luster.

Examples of the rubbery substance (B) used in the present invention included ethylene- $\alpha$ -olefin copoly-40 mer rubbers such as ethylene-propylene random copolymer and ethylene-propylene-diene random copolymer, natural rubber, isobutene rubber, butadiene rubber, 1,2-polybutadiene, styrene-butadiene random copolymer rubber, chloroprene rubber, nitrile rubber, styrene-butadiene-styrene block copolymer rubber, and styrene-isoprene-styrene block copolymer rubber. These rubbery substances may be used each alone or as mixtures. Particularly, ethylene-propylene-diene random copolymer rubber and ethylene-propylene random copolymer

45 rubber are preferred.

> The two rubbers just mentioned above, as compared with the other rubbery substances, are superior in thermoplasticity and can be easily dispersed by melt-kneading. Further, in comparison with SBR, isoprene rubber, nitrile rubber and butadiene rubber, they do not have any peculiar offensive odor and are easy to weigh and handle in mixing because they are available as pellets. Besides, the two rubbers in question have a large

50 degree of freedom in selecting a desired type of a composition preparing apparatus, thus having advantages in operation.

As to the diene component in the above ethylene-propylene-diene random copolymer rubber, it may be any of ethylidene norbornene, dicyclopentadiene, and 1,4-cyclohexadiene.

The Mooney viscosity of the rubbery substances exemplified above is preferably in the range of 55  $ML_{1+4}(100^{\circ}C) = 10$  to 100, more preferably  $ML_{1+4}(100^{\circ}C) = 20$  to 90. If  $ML_{1+4}(100^{\circ}C)$  is less than 10, the impact resistance will be scarcely improved and if ML<sub>1+4</sub>(100°C) is larger than 100, the dispersion of the rubbery substance used into the matrix resin will be poor.

The dihydroaromatic compound (D) used as a crosslinking agent in the present invention is a compound

containing one or more aromatic rings, of which at least one aromatic ring is dihydrogenated. The aromatic ring as referred to herein indicates a ring structure in which the number of  $\pi$ -electrons shown in the definition of aromaticity (see, for example, "Yuki Kagaku-No Kiso," Tokyo Kagaku Dojin K.K., translated by Toshio Goto,

- 5 (1974), pp.105-106) [Richard S. Mon-son & John C. Shelton, "Fundamentals of Organic Chemistry, "MacGraw-Hill, Inc. (1974)] is 4n + 2 (n is an integer). For example, pyridine and quinoline are included. Therefore, examples of the dihydroaromatic compound used in the present invention include dihydro derivatives of quinoline. Further, the dihydroaromatic compound used in the present invention may contain a substituent group. Alkyl substituted compounds as well as derivatives substituted with various elements or functional groups are em-
- ployable. The dihydroaromatic compounds employable in the present invention can be prepared by the application of known chemical reactions. Examples of such dihydroaromatic compounds now available include 1,2dihydrobenzene, cis-1,2-dihydrocatechol, 1,2-dihydronaphthalene, 9,10-dihydrophenanthrene, as well as 1,2dihydroquinoline compounds such as 6-decyl-2,2,4-trimethyl-1,2-dihydroquinoline, 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline, and 2,2,4-trimethyl-1,2-dihydroquinoline. Polymers of these compounds are also em-
- 15 ployable.

20

Among the dihydroaromatic compounds employable in the present invention there are those heretofore known as antioxidant agents (see, for example, Japanese Patent Publication No.46661/1980). However, these compounds have been used not as crosslinking agents but as ageing preventing agents together with conventional crosslinking agents such as sulfur compound, organic peroxides, phenolic compounds, or quinone-dioxime compounds.

Thus, the prior art is lacking in the knowledge of the present invention, namely, the knowledge that dihydroaromatic compounds and polymers thereof exhibit crosslinking reactivity, or the knowledge that a combined use of such dihydroaromatic compounds and polyfunctional monomers permits a mild crosslinking reaction to proceed.

- 25 The ether compound (E) used as a crosslinking agent in the present invention may be straight-chained or cyclic and may contain a substituent group. Examples are cyclic ethers such as 1,3-dioxolan and 3,4-dioxane; straight-chain ethers such as ethyl ether and isopropyl ether;non-aromatic cyclic vinyl ethers typified by 3,4-dihydro-2-pyran and 4H-chromene; furan derivatives typified by furfuryl alcohol, furfuryl aldehyde, benzofuran and furfuryl acetate; straight-chain vinyl ether compounds typified by n-octadecyl vinyl ether and ethyl vinyl
- 30 ether; and enol ethers and esters of carbonyl compounds such as ketone, esters, lactones, aldehydes, amides and lactams typified by ketene acetal, isopropenyl acetate, vinyl acetate and 1-amino-1-methoxyethylene. These compounds may contain substituent groups. Alkyl substituted compounds and derivatives substituted with various elements and functional groups are also employable. Further, these compounds may be used each alone or as mixtures. Particularly, vinyl and alkenyl ethers are preferred.
- <sup>35</sup> The tetrahydroaromatic compound (F) used as a crosslinking agent in the present invention is a compound in which at least one aromatic ring is tetrahydrogenated. The "aromatic ring" as referred to herein is of the same definition as that of aromaticity mentioned previously. For example, furan, benzene and naphthalene are included. Thus, examples of the tetrahydroaromatic compound used in the present invention include tetrahydro derivatives of naphthalene. Further, the tetrahydroaromatic compound used in the invention may contain a
- 40 substituent group. Alkyl substituted compounds as well as derivatives substituted with various elements or functional groups are also employable. The tetrahydroaromatic compounds employable in the present invention can be prepared by the application of known chemical reactions. Examples of those now available include 1,2,3,4-tetrahydronaphthalene, tetrahydrobenzene and tetrahydrofuran. Polymers of these compounds are also employable.
- 45 The cyclopentane compound (G) used as a crosslinking agent in the present invention indicates a compound which includes at least one cyclopentane, cyclopentene or cyclopentadiene skeleton. More specifically, it is a five-membered compound the ring of which is constituted by only carbon atoms. Examples include cyclopentane, cyclopentene, cyclopentadiene, dicyclopentadiene, indene, indane, and fluorene. These compounds may contain substituent groups. Alkyl substituted compounds as well as substituted derivatives using
- <sup>50</sup> various elements and functional groups are also employable. These compounds may be used each alone or as mixtures.

In the present invention it is necessary to use the component(s) (D), (E), (F) or (G), in combination with the polyfunctional monomer (C).

Examples of the polyfunctional monomer (C) include higher esters of methacrylic acid typified by trimethylolpropane trimethacrylate and ethylene glycol dimethacrylate; polyfunctional-vinyl monomers typified by divinylbenzene, triallyl isocyanurate and diallyl phthalate; and bismaleimides typified by N,N'-m-phenylene bismaleimide and N,N'-ethylene bismaleimide. Particularly, bismaleimide compounds and di(meth)acrylate compounds are preferred because these compounds are highly reactive and the addition of polar groups leads to the improvement in dispersibility and receptivity of inorganic fillers such as metal oxides for example. These

compounds may be used in combination of two or more.

Examples of the softening agent (H) used in the present invention are paraffinic, naphthenic and aromatic petroleum distillates components, and synthetic oils. Liquid polyisobutene may also be used .

As the inorganic filler (I) used in the present invention there may be used a known powdered, flat plate-

- 5 like, scale-like, needle-like, spherical, hollow, or fibrous inorganic filler. Examples are powdered fillers such as calcium carbonate, magnesium carbonate, calcium sulfate, siliceous sand calcium, clay, diatomaceous earth, talc, alumina, glass powder, iron oxide, metal powder, graphite, silicon carbide, silicon nitride, silica, bor-
- 10

15

on nitride, aluminum nitride, and carbon black; metallic foils such as mica, glass plate, sericite, pyrophyllite, and aluminum flake; flat plate-like or scale-like fillers such as graphite; hollow fillers such as Shirasu balloon, metal balloon, and pumice; and mineral fibers such as glass fibers, carbon fibers, graphite fibers, whisker, metal fibers, silicon carbide fibers, asbestos, and wollastonite.

These fillers maybe used each alone or as mixtures. The kind and the amount of the fillers(s) to be used may be determined according to the purpose of use. For the improvement of dispersibility it is desirable for these fillers to be surface-treated with a silane coupling agent, and organic titanate-based coupling agent, or a metallic salt of a fatty acid.

The partially crosslinked product used in the present invention is obtained by mixing the thermoplastic resin (A), the rubbery substance (B), the crosslinking agent (D), (E), (F) or (G) and the polyfunctional monomer (C) beforehand or at the time of heat treatment, and dynamically heat-treating the resulting mixture.

In the partially crosslinked composition thus obtained by the dynamic heat treatment, the boiling xylene insolubles content in the composition prepared by melt-kneading the said mixture is increased as compared with that before the kneading

As one criterion for the effect of the present invention there is mentioned such increase of the boiling xylene insolubles content attained by the heat treatment.

25

30

20

Generally, the larger the boiling xylene insolubles content, the more remarkable the improvement in the effect of addition of the rubbery substance, including the improvement of impact strength and tensile strength. A main factor of such increase in the boiling xylene insolubles content resides in the amount of the crosslinking agent and that of the polyfunctional monomer used, which amount differs depending on the kind of the crosslinking agent and that of the polyfunctional monomer used or the melt-kneading apparatus and conditions used.

The temperature of the foregoing dynamic heat treatment is not lower than the melting point or softening point of the C<sub>2</sub>-C<sub>8</sub>α-olefin (co)polymer and/or the rubbery substance and below the decomposition point thereof. Preferably, the dynamic heat treatment is conducted at a temperature of 120° to 350°C for 20 seconds to 20 minutes.

35

50

55

The melt kneading is preferably performed using a mixing machine which affords a high shear rate to facilitate the formation of radical in the mixture.

As the melt-kneading apparatus for the dynamic heat treatment there may be used any of known apparatus, including open type mixing rolls, non-open type Bumbury's mixer, extruder, kneader, and twin-screw extruder.

40 In preparing the partially crosslinked product used in the present invention it is necessary to use 40-90 wt% of the  $\alpha$ -olefin (co)polymer (A) having 2 to 8 carbon atoms, 10-60 wt% of the rubbery substance (B), 0.01-7 parts by weight, based on 100 parts by weight of the resin and rubbery substance, of at least one compound as a crosslinking agent selected from the dihydroaromatic compound or a polymer thereof (D), ether family compound (E), tetrahydroaromatic compound (F) and cyclopentane family compound (G), and 0.01-7 parts by 45 weight of the polyfunctional monomer (C) based on 100 parts by weight of the resin and the rubbery substance.

In the partially crosslinked product, if the amount of component (A) is smaller than 40 wt%, the resistance will be poor although the impact resistance will be improved.

If the amount of the crosslinking agent and that of the polyfunctional monomer are smaller than 0.01 part by weight, the crosslinking effect will be poor, and if they exceed 7 parts by weight, there will occur bleeding to the surface and coloration, thus causing increase of cost, in the case of the polyfunctional monomer, and coloration and increase of cost will result in the case. of the crosslinking agent.

In the case of using the softening agent (H), the amount thereof is in the range of 1 to 50, preferably 1 to 30, parts by weight based on 100 parts by weight of the resin and the rubbery substance. If the amount of the softening agent is smaller than 1 part by weight, the effect of improvement in fluidity will be poor, and if it exceeds 50 parts by weight, poor rigidity will result.

The softening agent may be added during and/or after the heat treatment in the total amount or in a suitably divided manner, but preferably it is melt-kneaded together with the other components at the time of the heat treatment.

Also, the inorganic filler (I) may be added during and/or after the heat treatment in the total amount or in

a suitably divided manner, but preferably it is melt-kneaded together with the other components in the heat treatment. This is desirable for enhancing the compatibility between the composition and the inorganic filler. The amount of the inorganic filler is in the range of 1 to 100, preferably 2 to 50, parts by the weight based

5 on 100 parts by weight of the resin and the rubbery substance. If the amount of the organic filler is smaller than 1 part by weight, the effect of its addition will not be satisfactory, and if it exceeds 100 parts by weight, deterioration will result in the tensile elongation and the appearance of molded products obtained.

It is important that the partially crosslinked product be contained in the composition of the present invention.

It is desirable that the content of the partially crosslinked product be at least 10 wt%, preferably not less than 20 wt%, more preferably not less than 30 wt%, based on the weight of the organic components.

As the resin incorporated in the partially crosslinked product there may be used the component (A) and/or the component (B). No special limitation is placed on the resin if only it is within the scope of the present invention.

The composition for vehicular exterior material in the third aspect of the present invention will be described in detail below.

The "vehicular exterior material" as referred to herein is of automobile including, for example, fender, door panel, protector, rear finisher, rear coater panel, engine hood, trunk lid, bumper fascia, energy absorber, air spoiler, side molding, weather strip, shock absorber, dust boots, vacuum connector, and rack and pinion boots.

- Recently, particularly in the automobile industry, the field in which plastics are used has been expanded, including automobile parts, and at the same time requirements have been diversified. For example, as to vehicular exterior materials, not only high heat resistance and low-temperature impact resistance are required but also excellence is required for moldability and the appearance of molded products (for example, good surface appearance is required, such as the absence of weld mark or flow mark) and also for coatability.
- 25

30

35

40

45

55

10

15

20

As a composition for such vehicular exterior materials satisfying the above requirements it is suitable to use the thermoplastic composition according to the present invention containing a partially crosslinked product which comprises, as the C<sub>2</sub>-C<sub>8</sub>  $\alpha$ -olefin (co)polymer, 40-90 wt% of a polypropylene resin (A<sub>1</sub>) and 0-30 wt% of a polyethylene resin (A<sub>2</sub>) (provided the total of A<sub>1</sub> + A<sub>2</sub> is in the range of 40 to 90 wt%), 10-60 wt% of the rubbery substance (B), at least one crosslinking agent selected from (D), (E), (F) and (G) and the polyfunctional monomer (C), or a thermoplastic resin composition comprising the said composition and the softening agent (H)

and/or the inorganic filler (I). These compositions are superior particularly as bumper materials. Suitable examples of the polypropylene resin (PP) include homopolypropylene, propylene-ethylene block copolymers, and propylene-butene-1 copolymer.

It is preferable that the propylene content in the above copolymers be not less than 60 wt%.

The melt flow rate (hereinafter referred to simply as "MFR") MFR of the above polypropylene is in the range of 5 of 50, preferably 6 to 45, more preferably 7 to 40. In the case of using a PP having a high MFR, due to a too great difference in viscosity in the melt kneading with the rubbery substance, it will be impossible to obtain a good dispersed state, so the resulting product will be inferior in impact resistance, having flow mark. If there is used a PP having a low MFR, there will be obtained only such a composition as having fluidity unsatisfactory for injection molding, and a bad weld mark will appear.

As preferred examples of the polyethylene resin  $(A_2)$  there are mentioned high-pressure process low-density polyethylenes, linear low-density polyethylenes and very-low density polyethylenes.

In the foregoing thermoplastic resin composition suitable for bumper, the proportion of the component  $(A_1)$  is in the range of 40 to 90 wt%, preferably 45 to 75 wt%, more preferably 50 to 70 wt%; the proportion of the component  $(A_2)$  is in the range of 0 to 30 wt%; and that of the component (B) is in the range of 10 to 60 wt%, preferably 25 to 55 wt%, more preferably 30 to 50 wt%.

If the proportion of the polypropylene resin as component ( $A_1$ ) is smaller than 40 wt%, the resulting composition will be poor in heat resistance, and if it exceeds 90 wt%, the impact resistance will be low.

In the composition for injection molding or the composition for vehicular exterior material according to the present invention, the partially crosslinked product containing the above polypropylene resin as a predominant ingredient and the rubbery substance is used as a main component. In this case, there may be added PP, etc. used in the component (A<sub>1</sub>) in an amount less than 50 wt%.

Bumpers of automobiles have been more and more diversified recently. Both hard and soft bumpers are used. As the material for hard bumpers it is desirable to use a composition obtained by incorporating 1-100 parts by weight of an inorganic filler into the above composition containing the partially crosslinked product. On the other hand, as the material for soft bumpers it is desirable to use a composition obtained by incorporating 1-50 parts by weight of the above composition containing the partially crosslinked product.

The vehicular exterior material constituted by the composition of the present invention is superior in heat resistance, impact resistance and coatability without deterioration in moldability and weld characteristic.

If necessary, into the composition of the present invention there may be incorporated stabilizer, antioxidant, ultraviolet ray absorber, lubricant, foaming agent, antistatic agent, flame retardant, dye, pigment, etc.

Thus in the present invention there are used a special crosslinking agent and a polyfunctional monomer in combination, the thermoplastic resin composition for injection molding according to the present invention is

superior in mechanical characteristics, e.g. rigidity, and in heat resistance, affording good appearance of product superior in gloss and free of such defects as flow mark and weld mark.

In the vehicular exterior material obtained according to the present invention, not only the above physical properties are retained but also, unlike the conventional crosslinking method using a peroxide, there does not occur any excessive molecular cuting (degradation) or crosslinking for polypropylene and rubber, and good dispersibility of the two ensures high heat resistance, impact resistance and coatability.

The present invention will be described below concretely in terms of working examples, but it is to be understood that the invention is not limited thereto.

15 Examples 1 - 20 and Comparative Examples 1 - 7

40-90 wt% of polypropylene resin ( $A_1$ ), 0-30 wt% of very-low density polyethylene ( $A_2$ ), 10-60 wt% of rubbery substance (B), 1-30 parts by weight of softening agent (H) and/or 1-17 parts by weight of inorganic filler (I), crosslinking agents (D), (E), (F) or (G) and polyfunctional monomer (C) were heat-treated dynamically. Test pieces were produced by injection-molding each composition and then annealing the resulting molded product,

unless otherwise described.

How to prepare compositions, conditions for producing test pieces by injection molding, and testing methods are as follows.

# 25 How to Prepare Compositions

Compositions were each prepared by:

1) mixing thermoplastic resin (A), rubbery substance (B), crosslinking agent (D), (E), (F) or (G) and polyfunctional monomer (C) in predetermined proportions by means of a Henschel mixer, provided in the case of further adding inorganic filler (I), mixing it together with the components (A) to (G), and

2) melt-kneading the resulting mixture at a resin temperature of 180° to 260°C and at a revolution of 200 rpm, using a continuous twin-screw extruder (30 mm dia., a product of Plastic Kogaku Kenkyu-Sho K.K.). Where the addition of a softening agent was required, it was poured using a reciprocating fixed displacement pump connected to a vent hole.

35

30

Conditions for Injection Molding

	Molding machine Injection pressure	: IS-90B (a product of Toshiba Machine Co., Ltd.) : 1,000 kg/cm <sup>2</sup>
Mold temperature : 50°C	40 Molding temperature	: 180-260°C

**Testing and Measuring Methods** 

45 (Melt Flow Rate)

According to JIS K6758 and K6760

# (Yield Tensile Strength, Ultimate Tensile strength and Ultimate Elongation Length)

50

According to JIS K6760, K6758 and K7113.

(Heat Deformation Temperature)

<sup>55</sup> According to JIS K7270, under a load of 4.6 kg.

(Flexural Modulus)

According to JIS K6758 and K7203.

10

20

(Izod Impact Value)

According to JIS K6758 and K7110.

5

10

(Boiling Xylene Insolubles Content)

A 20 mm x 50 mm x 0.2 mm film formed by pressing was placed in a 120-mesh wire gauze and then immersed in boiling xylene for 5 hours. The weight of the film before the immersion and that after the immersion were measure, and a boiling xylene insolubles content was obtained from the following equation:

Boiling xylene insolubles content (wt%) =  $\frac{\text{Weight (g) of film after immersion in boiling xylene}}{\text{Weight (g) of film before immersion in boiling xylene}} \times 100$ 

(Spiral Flow)

15

A sample is injected into a mold having a cavity of a predetermined spiral using the following molding conditions. The length of the spiral thus formed is measured for evaluating the melt-fluidity of the sample.

**Conditions of Injection Molding** 

20	

	Molding machine	: IS-90B (a product of Toshiba Machine Co., Ltd.)
	Injection pressure	: 1,000 kg/cm <sup>2</sup>
	Molding temperature	: 230°C
	Stroke	: 25 mm
25	Injection time	: 15 sec
	Curing time	: 10 sec
	Interval time	: 3 sec
	Mold	: Archimedes type, temp. 50°C

30 (Weld)

A sample is injected into a plane mold having a size of 80 mm x 240 mm x 3 mm and having a hole of 20 mm x 20 mm located at a position of 70 mm from the gate, using the following molding conditions and the molded article is evaluated by eye :

35

Conditions for Injection Molding

	Molding machine	: IS-90B (a product of Toshiba Machine Co., Ltd.)
	Injection pressure	: 1,000 kg/cm²
40	Molding temperature	: 180-260°C
	Mold temperature	: 50°C
	In the evaluation, A-	E is used in the order of merit (i.e. "A" indicates "best").

### (Flow Mark)

45

50

A sample is injected into a plane mold having a size of 100 mm x 200 mm x 3 mm using the following molding conditions and the molded article is evaluated by eye .

Conditions for Injection Molding

Molding machine	: IS-90B (a product of Toshiba Machine Co., Ltd.)
Injection pressure	: 1,000 kg/cm²
Molding temperature	: 230°C
Mold temperature	: 50°C
In the evaluation, A	E is used in the order of merit (i.e. "A" indicates "best").

55

(Face Impact Test (ductile fracture critical temp.))

According to Nisseki 3034-87

The components (A), (B), (C), (D) and (E) used in the working examples of the present invention and the Comparative examples are as follows:

5 Component (A): Polypropylene

(A<sub>1</sub>-1) Polypropylene (1) (trade name: Nisseki Polypro J650G, MRF=8.0 g/min, d=0.90~0.91 g/cm<sup>3</sup> a product of Nippon Petrochemicals Co., Ltd.)

 (A<sub>1</sub>-2) Polypropylene (2) (trade name: Nisseki Polypro J880G, MRF=40 g/min, d=0.90~0.91 g/cm<sup>3</sup>, a product of Nippon Petrochemicals Co., Ltd.)

(A<sub>1</sub>-3) Polypropylene (3)

(trade name: Nisseki Polypro J160G, MRF=14 g/min, d=0.90 $\sim$ 0.91 g/cm<sup>3</sup>, a product of Nippon Petrochemicals Co., Ltd.)

(A<sub>1</sub>-4) Polypropylene (4)

(trade name: Nisseki Polypro J871M, MRP=23 g/min, d=0.90 $\sim$ 0.91 g/cm<sup>3</sup>, a product of Nippon Petrochemicals Co., Ltd.)

20 Component (A<sub>2</sub>) : Very-Low Density Polyethylene

(A<sub>2</sub>-1) Very-low density polyethylene (1)

(trade name: Nisseki Softrex D9010, MRP=1.0 g/min, d=0.900 g/cm<sup>3</sup>, a product of Nippon Petrochemicals Co., Ltd.)

25 (A<sub>2</sub>-2) Very-low density polyethylene (2)

(trade name: Nisseki Softrex D9005, MRF=0.5 g/min, d=0.900 g/cm<sup>3</sup>, a product of Nippon petrochemicals Co., Ltd.)

Component (B) : Rubbery Substance

30

15

- (B<sub>1</sub>) Ethylene-propylene-diene random copolymer rubber (1) (trade name: EP57P, ML<sub>1+4</sub>(100°C)=88, a product of Japan Synthetic Rubber Co., Ltd.)
- (B<sub>2</sub>) Ethylene-propylene-diene random copolymer rubber (2) (trade name: EP 22, ML<sub>1+4</sub>(100°C)=42, a product of Japan Synthetic Rubber Co., Ltd.)
- <sup>35</sup> (B<sub>3</sub>) Ethylene-propylene random copolymer rubber (1)
  - (trade name: EP02P,  $ML_{1+4}(100^{\circ}C)=24$ , a product of Japan Synthetic Rubber Co., Ltd.) (B<sub>4</sub>) Ethylene-propylene random copolymer rubber (2)

(trade name: EP07P,  $ML_{1+4}(100^{\circ}C)=70$ , a product of Japan Synthetic Rubber Co., Ltd.)

<sup>40</sup> Crosslinking Agent

Component (D) : Dihydroaromatic Compound

- (D<sub>1</sub>) Poly (2,2,4-trimethyl-1,2-dihydroquinoline)
  - (trade name: Nocrac 224S, a product of Ohuchi Shinko Kagaku K.K.)
  - (D<sub>2</sub>) 9,10-Dihydrophenanthrene (a product of Tokyo Kasei K.k.)
- 50 Component (E) : Ether Family Compound

(E1) 3,4-Dihydro-2-pyran

(a product of Tokyo Kasei K.K.)

(E2) Isopropenyl acetate

(a product of Tokyo Kasei K.K.)

55

- Component (F) : Tetrahydroaromatic Compound
  - (F1) 1,2,3,4-Tetrahydronaphthalene

(a product of Tokyo Kasei K.K.) (F2) Tetrahydrobenzene (a product of Tokyo Kasei K.K.) (F3) Tetrahydrofuran (a product of Tokyo Kasei K.K.) Component (G) : Cyclopentane Family Compound 10 (G1) Indene Component (C) : Polyfunctional Monomer (C-1) N,N'-m-Phenylene bismaleimide (trade name: Vulnoc PM, a product Ohuchi Shinko Kagaku K.K.) 15 (C-2) Ethylene glycol dimethacrylate (a product of Tokyo Kasei K.K.) Component (H) : Softening Agent 20 Paraffinic process oil (a product of Nippon Oil Co., Ltd.) Component (I) : Inorganic Filler 25 Talc (trade name: TALC FFR, a product of Asada Seifun K.K.)

**Crosslinking Agent : Organic Peroxide** 

(J1) a, a'-Bis(t-butylperoxy)-m-diisopropylbenzene (trade name: Perbutyl P, a product of Nippon Oils & 30 Fats Co., Ltd.)

35

5

40

45

50

Table l Examples l - 8, Comparative Examples l - 3 (1/2)

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Iten				Ŭ	Composition						Physica	Physical Properties	
Kind         Amount         Kind         Ki		CO CO	onent A	Comp	onent B	Filler	Gros Agel	s linking nt	Polyfi monome	Inctional	Melt Flow Rate (g/10 min) (at 230°C)	Spiral Flow	Yield Tensile Strength	Ultimate Tensil at Break
A-1         62         B1         30         17         D1         1.50         C1         1.80         B.0         690           A1-2         72         B2         28         11         D2         0.12         C1         0.1         7.0         660           A1-2         72         B2         28         11         D2         0.12         C1         0.1         7.0         660           A1-3         74         B4         26         11         B2         0.12         C2         0.1         7.0         680           A1-1         70         B2         30         2         F1         0.12         C2         0.1         7.0         680           A1-1         40         B2         11         B2         0.12         C1         0.1         10         800           A1-1         45         B1         55         D1         0.42         C2         0.1         16         800           A1-3         75         B1         55         D1         0.42         C2         0.1         16         800           A1-3         75         B1         0.42         C2         0.4	Example	Kind	Amount (wt%)	Kind	Amount (wt%)	Amount (wt part)		Amount (wt part)	1	Amount (wt part)		( mm )	(kgf/cm <sup>2</sup> )	(kgf/cm <sup>2</sup> )
A1-2       72       B2       28       11       D2       0.12       C1       0.1       7.0       660         A1-3       74       B4       26       11       B2       0.12       C2       0.1       7.0       660         A1-1       70       B2       21       5       E1       0.12       C2       0.1       7.0       680         A1-1       70       B2       30       2       F1       0.12       C2       0.1       10       800         A1-1       70       B2       30       2       F1       0.12       C2       0.1       10       800         A1-3       75       B1       25       11       F3       0.12       C1       0.1       16       860         A1-3       75       B1       55       25       D1       0.42       C2       0.4       0.5       -       -       -       45       -       0       0       0       <	Example 1	A-1 A2	62 8	B1	30	17	D1	1.50	C1	1.80	B.0	690	170	110
A1-2       79       B3       21       5       E1       0.12       C2       0.1       7.0       680         A1-3       74       B4       26       11       B2       0.12       C1       0.1       7.0       680         A1-1       70       B2       30       2       F1       0.12       C1       0.1       10       800         A1-1       70       B2       30       2       F2       0.08       C1       0.1       10       800         A1-1       60       B3       20       5       F2       0.08       C1       0.1       16       860         A1-3       75       B1       25       D1       0.42       C2       0.1       16       860         A1-3       75       B1       55       25       D1       0.42       C2       0.4       0.5          A1-3       76       B2       25       D1       0.42       C2       0.4       0.5        -       45        -       -       45        -       -       45        -       -       45        -       45		A1-2	72	B2	28	11	D2	0.12	CI	0.1	7.0	660	200	>175
A1-3       74       B4       26       11       B2       0.12       C1       0.1       3.2       590         A1-1       70       B2       30       2       F1       0.12       C2       0.1       10       800         A1-1       80       B3       20       5       F2       0.08       C1       10       800         A1-3       75       B1       25       11       F3       0.12       C1       0.1       16       860         A1-3       75       B1       25       11       F3       0.12       C1       0.1       16       860         A1-3       75       B1       55       25       D1       0.42       C2       0.4       0.5          A1-3       65       B1       35       11       D1       0.42       C2       0.4       0.5          A1-3       76       B2       25       11       D1       0.42       C2       0.4       0.5          A1-3       76       B2       25       11       J1       0.2        45           A1-1       72		A1-2	19	B3	21	S	Е1	0.12	C	0.1	7.0	680	215	>187
Al-1       70       B2       30       2       F1       0.12       C2       0.1       10       800         Al-1       60       B3       20       5       F2       0.08       C1       0.1       16       860         Al-3       75       B1       25       11       F3       0.12       C1       0.1       3.5       600         Al-1       45       B1       55       25       D1       0.42       C2       0.4       0.5          Al-3       65       B1       35       11       D1       0.42       C2       0.4       0.5        -         Al-3       75       B1       55       25       D1       0.42       C2       0.4       0.5        -	Example 4	A1-3	14	84	26	11	Ε2	0.12	Ċ1	0.1	3.2	290	186	>168
A1-1       80       B3       20       5       F2       0.08       C1       0.1       16       860         A1-3       75       B1       25       11       F3       0.12       C1       0.1       3.5       600         A1-1       45       B1       55       25       D1       0.42       C2       0.4       0.5          A1-3       65       B1       35       11       D1       0.42       C2       0.4       0.5          A1-3       75       B1       35       11       D1       0.42       C2       0.4       0.5          A1-3       75       B1       35       11       D1       0.42       C1       8.0       1.1       500         A1-1       72       B1       28       11       J1       0.2        45          A1-1       72       B1       28       11       J1       0.2        14       790		A1-1	70	B2	30	2	F1	0.12	ß	0.1	10	800	188	>170
A1-3       75       B1       25       11       F3       0.12       C1       0.1       3.5       600         A1-1       45       B1       55       25       D1       0.42       C2       0.4       0.5          A1-3       66       B1       35       11       D1       0.42       C2       0.4       0.5          A1-3       65       B1       35       11       D1       0.42       C2       0.4       0.5          A1-3       75       B2       25       11       J1       0.2        45          A1-1       72       B1       28       11       J1       0.2        45          A1-1       72       B1       28       11       J1       0.2        45		A1-1	80	B3	20	ŝ	F 2	0.08	CI	0.1	16	860	223	>195
A1-1         45         B1         55         25         D1         0.42         C2         0.4         0.5            A1-3         65         B1         35         11         D1         0.42         C2         0.4         0.5            A1-3         65         B1         35         11         D1         0.0         C1         8.0         1.1         500           A1-3         75         B1         25         11         J1         0.2          45            A1-1         72         B1         28         11          14         790	Example 7	A1-3	75	B1	25	11	F 3	0.12	CI	0.1	3.5	600	188	>170
A1-3     65     B1     35     11     D1     8.0     C1     8.0     1.1     500       A1-3     75     B2     25     11     J1     0.2      45        A1-1     72     B1     28     11     J1     0.2      14     790	Example 8	A1-1	4 5	B1	55	25	D 1	0.42	C2	0.4	0.5		130	100
A1-3         65         B1         35         11         D1         6.0         C1         8.0         1.1         500           A1-3         75         B2         25         11         J1         0.2         -         45         -         45         -           A1-1         72         B1         28         11         J1         0.2         -         -         45         -	Comparative													
Al-1 72 B1 28 11 J1 0.2 - 45 - 14 790	Example 1	A1-3	65	B1	35	11	Ħ	8.0	C1	9.0	1.1	500	110	>100
2         A1-3         75         B2         25         11         J1         0.2         -         45         -           cive         3         A1-1         72         B1         28         11         0.2         -         45         -         -         45         -         -         45         -         -         45         -         -         45         -         -         -         45         -         -         -         45         -         -         45         -         -         -         45         -	Gomparative													
ive :: 14 72 B1 28 11 14 790	Example 2	A1-3	75	B2	25	11	11	0.2			. 45		170	>150
3 A1-1 72 B1 28 11 14 790	Comparative													
	Example 3	A1-1	72	<b>B</b> 1	28	11		-		1	14	06L	170	>152

Table 1 Examples 1 - 8, Comparative Examples 1 - 3 (2/2)

	Item				lya	Physical Properties	ea			
LengthLength $-40^{\circ}$ Ccritical temperature(x) $(kgf/cm^2)$ $(kgf/cm^2)$ $(^{\circ}$ C) $(tcc)$ $ture$ )230235 $14,000$ 122 $7.5$ $-21$ CB>500131 $12,700$ 112 $8.9$ $-230$ AB>500131 $12,700$ 112 $8.9$ $-21$ CB>500130135 $7.0$ $-21$ BBA>50013013,000119 $9.1$ $-300$ BBB>50013013,000119 $9.1$ $-30$ BBB>50013213,000110 $6.9$ $-23$ BBB>50013210,000110 $6.9$ $-23$ BBB>50011710,000100 $9.300$ $96$ $10.0$ $-30$ BDD>500117 $10,000$ 103 $2.5$ $-10$ $B$ BB>500117 $10,000$ 103 $2.6$ $-10$ BDD>500117 $10,000$ 103 $2.6$ $-10$ BCB>500117 $10,000$ 100 $100$ $4.0$ $-10$ BDD	•	Ultimate Blongation		Flexural Modulus	Vicat Soften- ing Point	Izod Impact Test	Face Impact Test (ductile fracture	Weld Mark Evaluation	Flow Mark Evaluation	Boiling Xylene
(x)         (kgf/cm <sup>2</sup> )         (rc)         (kgf.cm/cm)         (rc)         (rgf.cm/cm)         (rc)         (rgf.cm/cm)         (rc)         (rd)         (rc)         (rc)         (rc)         (rc)         (rc) $rc$ $rd$		Length				-40°C	critical tempera- ture)			<b>Ins</b> olubles Content
230       235       14,000       122       7.5       -21       C       B         >500       131       12,700       112       8.9       -30       A       B         >500       136       12,800       105       8.0       -21       B       B       B         >500       130       12,800       106       8.0       -21       B       B       B         >500       130       12,800       106       8.0       -25       B       B       B         >500       130       130       119       9.1       -300       B       B       B         >500       131       13,000       119       9.1       -30       B       B       B         >500       132       13,000       110       6.9       -23       B       B       B         >500       132       13,000       110       6.9       -23       B       B       B         >500       132       13,000       10       11.2       11.2       10.0       B       B       B         >500       13       9.300       96       10.0       -30       B       B       B	Example	(%)	(kgf/cm <sup>2</sup> )	(kgf/cm <sup>2</sup> )		(kgf.cn/cm)				(%)
>500       131       12,700       112       8.9       -30 <b>A B</b> >500       146       13,000       135       7.0       -21 <b>B B B</b> >500       130       12,800       105       9.0       -25 <b>B A</b> >500       130       12,800       105       9.0       -25 <b>B A</b> >500       130       13,000       136       9.1       -30 <b>B B A</b> >500       130       13,000       136       7.0       -15 <b>B B B</b> >500       132       13,000       110       6.9       -23 <b>B B B</b> >700       90       7,600       -11.2       -115 <b>D D D D</b> >500       117       10,000       103       2.5       -16 <b>B B B</b> >500       117       10,000       103       2.5       -10 <b>B B B</b> >500       117       10,000       103       2.6       -10 <b>B</b>	Example 1	230	235	14,000		7.5	-21	U	£	38
>500       146       13,000       135       7.0       -21       B       B       A         >500       130       12,800       106       8.0       -25       B       A       A         >500       130       12,800       106       9.1       -25       B       A       C         >500       130       13,000       136       7.0       -15       A       C         >500       132       13,000       110       6.9       -15       A       C         >500       132       13,000       110       6.9       -23       B       B       B         >770       80       7,600        11.2       -11.2       D       D       D         >500       97       9,300       96       10.0       -15       D       D       D         >500       117       10,000       103       2.5       -110       B       B       D         >500       120       11,000       100       100       4.0       -10       B       C	Example 2	>500	131	12,700	112	ດ. ຍ	-30	¥	£	34
>500       130       12,800       106       8.0       -25       B       A         >500       120       10,500       119       9.1       -30       B       B       B         >500       130       13,000       136       7.0       -15       A       C         >500       132       13,000       110       6.9       -23       B       B       B         >500       132       13,000       110       6.9       -23       B       B       B         >700       90       7,600       -11.2       11.2       -15       D       D       D         >500       117       10,000       100       2.5       -16       B       B       D         >500       117       10,000       103       2.5       -10       B       D       D         >500       117       10,000       103       2.5       -10       B       D       D         >500       110       10,000       100       4.0       -10       B       D       D		>500	146	13,000	135	7.0	-21	B	ß	20
>500       120       10,500       119       9.1       -30       B       B       B         >500       150       13,000       136       7.0       -15       A       C         >500       132       13,000       136       7.0       -15       A       C         >500       132       13,000       110       6.9       -23       B       B       B         >500       97       9,300       96       10.0       -30       B       D       D       D         >500       117       10,000       103       2.5       -10       B       B       D       D         >500       120       11,000       103       2.5       -10       B       C       C	Example 4	> 500	130	12,800	106	8.0	-25	63	¥	26
>500       150       13,000       136       7.0       -15       A       C         >500       132       13,000       110       6.9       -23       B       B       B         270       80       7,600        11.2       -15       D       D       D         >500       97       9,300       96       10.0       -30       B       D       D         >500       117       10,000       103       2.5       -10       B       D       D         >500       120       11,000       103       2.5       -10       B       B       D         >500       120       11,000       100       4.0       -10       B       C       C		>500	120	10,500	119	9.1	- 30	B	£	30
>500       132       13,000       110       6.9       -23       B       B         270       80       7,600        11.2      15       D       D       D         >500       97       9,300       96       10.0       -30       B       D       D         >500       117       10,000       103       2.5       -10       B       B       D         >500       117       10,000       103       2.5       -10       B       B       D         >500       120       11,000       100       4.0       -10       B       C       C		> 500	150	13,000	136	7.0	-15	V	υ	17
270     80     7,600      11.2     -15     D     D       >500     97     9,300     96     10.0     -30     B     D       >500     117     10,000     103     2.5     -10     E     E       >500     120     11,000     100     4.0     -10     E     C	Example 7	. >500	132	13,000	110	6.9	-23	8	Ð	31
>500     97     9,300     96     10.0     -30     B     D       >500     117     10,000     103     2.5     -10     B     B       >500     120     11,000     100     4.0     -10     B     C	Example 8	270	80	1,600		11.2	-15	a	٥	60
>500     97     9,300     96     10.0     -30     B     D       >500     117     10,000     103     2.5     -10     E     E       >500     120     11,000     100     4.0     -10     E     C	Comparative									
>500         117         10,000         103         2.5         -10         E         E           >500         120         11,000         100         4.0         -10         E         C	Example 1	> 500	97	9,300	36	10.0	-30	æ	۵	41
>500     117     10,000     103     2.5     -10     E     E       >500     120     11,000     100     4.0     -10     E     C	Comparative				·			I		ļ
>500 120 11,000 100 4.0 -10 B C	Example 2	> 500	117	10,000	103	2.5	-10	2	M	97
3 >500 120 11,000 100 4.0 -10 B C	Comparative			•					I	
		>500	120	11,000	100	4.0	-10	24	C	10

15
20
25
30
35

45

50

55

5

10

Table 2 Examples 9 - 21, Comparative Examples 4 - 7 (1/2)

(kgf/cm<sup>2</sup>) Strength Tensile Yield 140 145 130 110 140 110 160 140 140 145 140 170 175 140 88 Physical Properties Spiral (mm) 640 Flow 520 580 860 650 660 660 660 700 700 820 600 420 450 Rate (g/10 min) (at 230°C) Melt Flow 2.5 2.0 0.6 0.4 3.2 0.7 1.2 0.4 0.7 0.8 2.0 0.5 0.1 0.1 10 12 Polyfunc-(wt part) nonomer Amount tional ( C1) 0.60 0.60 0.60 0.60 0.20 1.80 0.60 0.60 0.10 0.30 0.60 0.60 8.00 0.60 0 (wt part) Crosslinking Amount 0.50 0.50 0.50 0.50 0.20 1.50 0.50 0.50 0.30 0.08 0.50 8.00 0.30 0.50 0 . Agent Kind D1 5 ā In Comparative Examples 1 and 5, white powder was formed on the surface. (wt part) Softening Amount 20 5 20 20 20 20 20 20 20 20 20 20 20 20 20 0 20 20 20 Agent Amount (wt%) 10 Composition (Y) kind - ~ Asount (wt%) 35 35 35 35 E) Kind 83 81 B1 B1 Amount (wt%) 65 65 65 65 ( I V ) Kind ---3 2 3 -------- -----Item Comparative Comparative Comparative Comparative o, 2 11 12 13 1 15 16 17 18 Example 4 Example 5 Example 6 Example 7 19 20 Example Example

14

<u>xamples 4 - 7 (2/2)</u>
Comparative E
9 - 21,
Examples
Table 2

Item				Physic	Physical Properties				
	Ultimate Elongation Length	Bending Strength	Flexural Modulus	Vicat Soften- ing Point	Izod Impact Test -40°G	Face Impact Test (ductile fracture critical tempera- ture)	Weld Mark Evaluation	Flow Mark Evaluation	Boiling Xylene Insolubles Content
Example	(%)	(kgf/cm <sup>2</sup> )	Ž		(kgf.cm/cm)	(D.)	4	A	(%) 25
Example 9	580	06	3,050	6	G Z	-30	. ea	B	32
Example 10	590	06	3,100	* * 5	EN .	-30	E	æ	•
EXample 11 Example 12	480	06	3,070	46	19	-25	<b>4</b>	α α	12
Example 13	420	110	3,700	103	13	-20	K 4	2 4	16
Example 14	380	110	3,800	105	11	07-	: @	¥	11
Example 15	570	06	3,100	06	<u>6</u> 1 -	-20	Ω.	£	30
Example 16	580	120	4,200	110		- 25	đ	ß	10
Example 17	580	95	3,200	96	0 1	06-	8	4	10
Example 18	580	100	3,400	<b>6</b> 6	6 I	01-	. U	U	10
Example 19	300	180	6,300	122	o 9	5 T	-	8	23
Example 20	320	54	1,200	62	13				
Comparative Example 4	590	105	3,700	87	æ	-20	EI	£	-
Comparative				6	23	-25	#	B	30
Example 5	580	06	۰، ۱	, ,					
Comparative Example 6	580	85	2,800	06	12	-20	с 	ы	34
	0	175	6,150	125	10	-20	B	U	34
The Comparative Examples 1	re Examples 1	and 5, v	ite powder	white powder was formed on the	the surface.				

# Claims

5

10

15

20

50

- 1. An external component for a vehicle which is molded from a composition comprising a partially crosslinked product, said partially crosslinked product being prepared by dynamically heat-treating:
  - (A) 40-90% by weight of an  $\alpha$ -olefin (co)polymer resin having 2 to 8 carbon atoms;
  - (B) 10-60% by weight of a rubbery substance;
  - (C) 0.01-7 parts by weight of a polyfunctional monomer based on 100 parts by weight of said components (A)+(B); and

0.01-7 parts by weight, based on 100 parts by weight of said components (A)+(B), of at least one crosslinking agent selected from:

- (D) a dihydroaromatic compound or a polymer thereof,
- (E) an ether compound,
- (F) a tetrahydroaromatic compound, and
- (G) a cyclopentane compound.
- 2. A component according to claim 1 wherein the composition additionally comprises:
  - (H) 1-30 parts by weight of a softening agent;
    - (I) 1-100 parts by weight of an inorganic filler; or

(J) 1-30 parts by weight of a softening agent and 1-100 parts by weight of an inorganic filler; based on 100 parts by weight of the partially crosslinked product.

- 3. A component according to Claim 1 or 2 wherein said  $\alpha$ -olefin (co)polymer (A) having 2 to 8 carbon atoms is at least one of polyethylene resins, polypropylene resins and poly-1-butene resins.
  - **4.** A component according to any one of Claims 1 to 3 wherein said rubbery substance (B) is an ethylenepropylene random copolymer rubber or an ethylene-propylene-diene random copolymer rubber.
- <sup>30</sup> 5. A component according to any one of Claims 1 to 4 werein said dihydroaromatic compound (D) is a 1,2-dihydroquinoline compound or a polymer thereof, or 9,10-dihydrophenanthrene; the ether compound (E) is dihydropyran or isopropenyl acetate; the tetrahydroaromatic compound (F) is 1,2,3,4-tetrahydronaph-thalene, tetrahydrobenzene, or tetrahydrofuran, and the cyclopentane compound (G) is indene.
- <sup>35</sup> **6.** A component as set forth in any of Claims 1 to 5, wherein said polyfunctional monomer (C) is a bismaleimide compound or a di(meth)acrylate compound.
  - 7. A component as set forth in any of Claims 2 to 6, wherein said softening agent (H) is at least one of paraffinic, naphthenic and aromatic petroleum distillates and synthetic oils.
- A component as set forth in any of Claims 1 to 7, wherein said α-olefin (co)polymer (A) having 2 to 8 carbon atoms comprises:

(A-1) 40-90% by weight of a polypropylene resin, and

- (A-2) 0-30% by weight of a polyethylene resin,
- 45 provided the total amount of A1+A2 is in the range of 40% to 90% by weight.
  - **9.** A composition suitable for use in an external component for a vehicle comprising a partially crosslinked product, said partially crosslinked product being prepared by dynamically heat-treating:
    - (A) 40-90% by weight of an  $\alpha$ -olefin (co)polymer resin having 2 to 8 carbon atoms;
    - (B) 10-60% by weight of a rubbery substance;
    - (C) 0.01-7 parts by weight of a polyfunctional monomer based on 100 parts by weight of said components (A)+(B); and
    - 0.01-7 parts by weight, based on 100 parts by weight of said components (A)+(B), of at least one crosslinking agent selected from:
- 55 (E) an ether compound,
  - (F) a tetrahydroaromatic compound, and
  - (G) a cyclopentane compound.
  - **10.** A composition according to claim 9 wherein the composition additionally comprises:

- (H) 1-50 parts by weight of a softening agent;
- (I) 1-100 parts by weight of an inorganic filler; or
- (J) 1-50 parts by weight of a softening agent and 1-100 parts by weight of an inorganic filler based on
- 100 parts by weight of the partially crosslinked product.

# Patentansprüche

5

15

20

25

35

40

45

50

55

- 10 1. Externe Komponente für einen Trägerstoff, der aus einer ein teilvernetztes Produkt umfassenden Zusammensetzung geformt wird, wobei dieses teilvernetzte Produkt durch dynamische Wärmebehandlung von
  - (A) 40 90 Gew.% eines  $\alpha$ -Olefin-(Co)polymerharzes mit 2 bis 8 Kohlenstoffatomen;
  - (B) 10 60 Gew.% einer kautschukartigen Substanz;
  - (C) 0,01 7 Gewichtsteilen eines polyfunktionellen Monomers bezogen auf 100 Gewichtsteile der Komponenten (A) und (B); und
    - 0,01 7 Gewichtsteilen, bezogen auf 100 Gewichtsteile der Komponenten (A) und (B), mindestens eines Vernetzungsmittels, das ausgewählt ist aus
      - (D) einer dihydroaromatischen Verbindung oder einem Polymer davon,
      - (E) einer Etherverbindung,
  - (F) einer tetrahydroaromatischen Verbindung und
    - (G) einer Cyclopentanverbindung

hergestellt wird.

- 2. Komponente nach Anspruch 1, in der die Zusammensetzung außerdem
  - (H) 1 30 Gewichtsteile eines Weichmachers;
    - (I) 1 100 Gewichtsteile eines anorganischen Füllstoffs oder

(J) 1 - 30 Gewichtsteile eines Weichmachers und 1 - 100 Gewichtsteile eines anorganischen Füllstoffs bezogen auf 100 Gewichtsteile des teilvernetzten Produkts enthält.

- 3. Komponente nach Anspruch 1 oder 2, in der das  $\alpha$ -Olefin-(Co)polymer (A) mit 2 bis 8 Kohlenstoffatomen Polyethylenharz, Polypropylenharz und/oder Polybut-1-enharz ist.
  - 4. Komponente nach einem der Ansprüche 1 bis 3, in der die kautschukartige Substanz (B) ein Kautschuk aus Ethylen-Propylen statistischem Copolymer oder ein Kautschuk aus Ethylen-Propylen-Dien statistischem Copolymer ist.
  - 5. Komponente nach einem der Ansprüche 1 bis 4, in der die dihydroaromatische Verbindung (D) eine 1,2-Dihydrochinolin-Verbindung, ein Polymer davon oder 9,10-Dihydrophenanthren, die Etherverbindung (E) Dihydropyran oder Isopropenylacetat, die tetrahydroaromatische Verbindung (F) 1,2,3,4-Tetrahydronaphthalin, Tetrahydrobenzol oder Tetrahydrofuran und die Cyclopentanverbindung (G) Inden ist.
  - 6. Komponente nach einem der Ansprüche 1 bis 5, in der das polyfunktionelle Monomer (C) eine Bismaleinimid- oder eine Di(meth)acrylatverbindung ist.
  - 7. Komponente nach Anspruch 2 bis 6, in der der Weichmacher (H) ein paraffinisches, naphthenisches oder aromatisches petroleumdestillat und/oder ein synthetisches Öl ist.
  - **8.** Komponente nach einem der Ansprüche 1 bis 7, in der das α-Olefin-(Co)polymer (A) mit 2 bis 8 Kohlenstoffatomen
    - (A-1) 40 90 Gew.% Polypropylenharz und
    - (A-2) 0 30 Gew.% polyethylenharz

umfaßt, vorausgesetzt, die Gesamtmenge von A1 + A2 ist im Bereich von 40 bis 90 Gew.%.

**9.** Zusammensetzung, die geeignet ist zur Verwendung als externe Komponente für einen Trägerstoff, der ein teilvernetztes Produkt umfaßt, das durch dynamische Wärmebehandlung von

(A) 40 - 90 Gew.% eines  $\alpha$ -Olefin-(Co)polymerharzes mit 2 bis 8 Kohlenstoffatomen;

(B) 10 - 60 Gew.% einer kautschukartigen Substanz;

(C) 0,01 - 7 Gewichtsteilen eines polyfunktionellen Monomers bezogen auf 100 Gewichtsteile der Komponenten (A) und (B); und

0,01 - 7 Gewichtsteilen, bezogen auf 100 Gewichtsteile der Komponenten (A) und (B), mindestens eines

- Vernetzungsmittels, das ausgewählt ist aus
- (E) einer Etherverbindung,
- (F) einer tetrahydroaromatischen Verbindung und
- (G) einer Cyclopentanverbindung
- hergestellt wird.
- **10.** Komponente nach Anspruch 1, in der die Zusammensetzung außerdem
  - (H) 1 50 Gewichtsteile eines Weichmachers;
  - (I) 1 100 Gewichtsteile eines anorganischen Füllstoffs oder
    - (J) 1 50 Gewichtsteile eines Weichmachers und
    - 1 100 Gewichtsteile eines anorganischen Füllstoffs bezogen auf 100 Gewichtsteile des teilvernetzten Produkts
  - enthält.

20

25

30

35

5

10

# Revendications

- Composant externe pour un véhicule qui est moulé à partir d'une composition comprenant un produit partiellement réticulé, ce produit partiellement réticulé étant préparé par traitement à chaud de façon dynamique de:
  - (A) 40 à 90% en poids d'une résine (co)polymère d'α-oléfine ayant 2 à 8 atomes de carbone;
  - (B) 10 à 60% en poids d'une substance caoutchouteuse;
  - (C) 0,01 à 7 parties en poids d'un monomère polyfonctionnel pour 100 parties en poids de ces composants (A) + (B); et
  - 0,01 à 7 parties en poids pour 100 parties en poids de ces composants (A) + (B), d'au moins un agent de réticulation choisi parmi :
    - (D) un composé dihydroxyaromatique ou un polymère de celui-ci,
    - (E) un composé éther,
    - (F) un composé tétrahydroaromatique et
    - (G) un composé cyclopentane.
- 2. Composant suivant la revendication 1, dans laquelle la composition comprend de plus :
  - (H) 1 à 30 parties en poids d'un agent plastifiant;
  - (I) 1 à 100 parties en poids d'une charge inorganique; ou
  - (J) 1 à 30 parties en poids d'un agent plastifiant et 1 à 100 parties en poids d'une charge inorganique; pour 100 parties en poids du produit partiellement réticulé.
- Composant suivant les revendications 1 ou 2, dans lequel ce (co)polymère d'α-oléfine (A) ayant 2 à 8 atomes de carbone est au moins l'une des résines polyéthylènes, résines polypropylènes et résines polpy-1-butènes.
  - 4. Composant suivant l'une quelconque des revendications 1 à 3, dans lequel cette substance caoutchouteuse (B) est un caoutchouc copolymère statistique d'éthylène et de propylène ou un caoutchouc copolymère statistique d'éthylène, de propylène et d'un diène.
- 45

- 5. Composant suivant l'une quelconque des revendications 1 à 4, dans lequel ce composé dihydroxyaromatique (D) est un composé 1,2-dihydroquinoléine ou un polymère de celui-ci, ou le 9,10-dihydrophénanthrène; le composé éther (E) est le dihydropyrane ou l'acétate d'isopropényle; le composé tétrahydroaromatique (F) est le 1,2,3,4-tétrahydronaphtalène, le tétrahydrobenzène ou le tétrahydrofurane, et le composé cyclopentane (G) est l'indène.
- 6. Composant suivant l'une quelconque des revendications 1 à 5, dans lequel ce monomère polyfonctionnel (C) est un composé bismaléimide ou un composé di(méth)acrylique.
- **7.** Composant suivant l'une quelconque des revendications 2 à 6, dans lequel cet agent plastifiant (H) est au moins un agent choisi parmi les distillats de pétrole paraffiniques, naphténiques et aromatiques et les huiles de synthèse.
  - 8. Composant suivant l'une quelconque des revendications 1 à 7, dans lequel ce (co)polymère d'α-oléfine

- (A) ayant 2 à 8 atomes de carbone comprend:
  - (A-1) 40 à 90% en poids d'une résine polypropylène, et
  - (A-2) 0 à 30% en poids d'une résine polyéthylène,
- 5 à condition que la quantité totale de (A-1) + (A-2) soit comprise entre 40% et 90% en poids.
  - 9. Composition utilisable dans un composant externe pour un véhicule comprenant un produit partiellement réticulé, ce produit partiellement réticulé étant préparé par traitement à chaud de façon dynamique de:

     (A) 40 à 90% en poids d'une résine (co)polymère d'α-oléfine ayant 2 à 8 atomes de carbone;
    - (B) 10 à 60% en poids d'une substance caoutchouteuse;
      - (C) 0,01 à 7 parties en poids d'un monomère polyfonctionnel pour 100 parties en poids de ces composants (A) + (B); et
      - 0,01 à 7 parties en poids pour 100 parties en poids de ces composants (A) + (B), d'au moins un agent de réticulation choisi parmi :
  - (E) un composé éther,
    - (F) un composé tétrahydroaromatique et
    - (G) un composé cyclopentane.
    - 10. Composition suivant la revendication 9, dans laquelle la composition comprend de plus :
    - (H) 1 à 50 parties en poids d'un agent plastifiant;
      - (I) 1 à 100 parties en poids d'une charge inorganique; ou
      - (J) 1 à 50 parties en poids d'un agent plastifiant et 1 à 100 parties en poids d'une charge inorganique; pour 100 parties en poids du produit partiellement réticulé.

25

10

15

20

30

35

45

50